



2000

# The Synthesis of Hybrid Materials by the Blending of Polyhedral Oligosilsesquioxanes into Organic Polymers

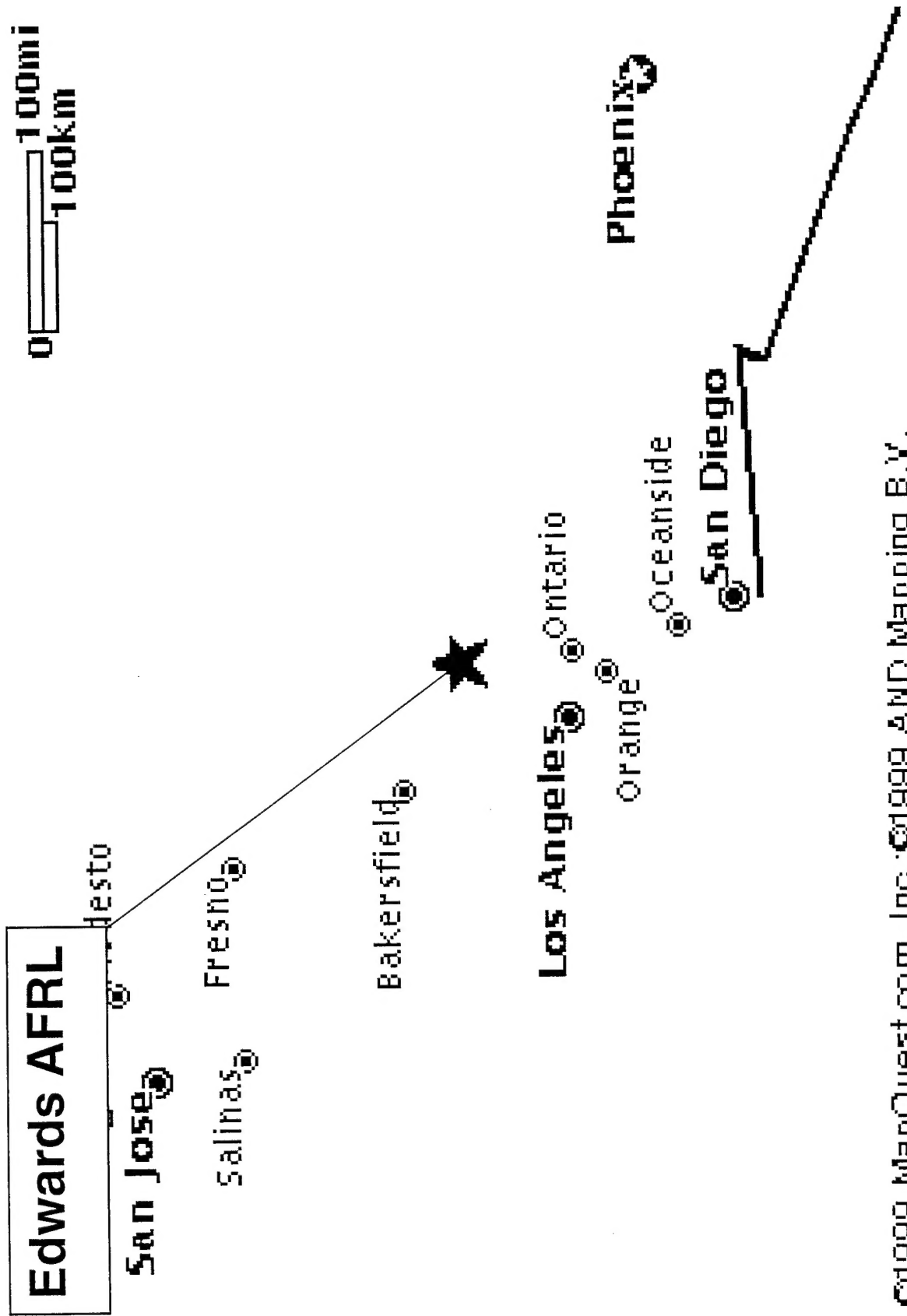
Rusty L. Blanski<sup>1</sup>, Shawn H. Phillips<sup>1</sup>, Kevin Chaffee<sup>1</sup>, Joseph  
Lichtenhan<sup>2</sup>, Andre Lee<sup>3</sup>, and Hei Ping Geng<sup>3</sup>.

<sup>1</sup>AFRL/PRSM, Air Force Research Laboratory, 10 E. Saturn Blvd,  
Bldg. 8451, Edwards AFB, CA 93524,

<sup>2</sup>Hybrid Plastics, 18237 Mt. Baldy Circle, Fountain Valley, CA  
92708

<sup>3</sup>Department of Materials Science and Mechanics, Michigan State  
University, East Lansing, MI 48824

20000830 082





# Hybrid Organic/Inorganic Blends

- GOAL: To study the interaction and solubility of Polyhedral Oligosilsesquioxane (POSS) molecules containing various organic side groups with the polymer matrix
- Polystyrene was chosen since it is readily available and can easily be solvent cast with the POSS molecules for TEM studies



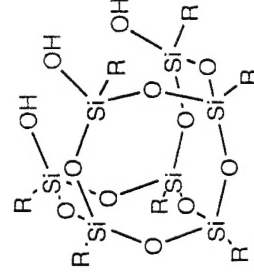
# Why Use Blendables?

- Easier to tailor the organic side groups of the POSS molecule to give a polymer-soluble species
- Simple blending techniques can be used instead of copolymerization with reactive POSS monomers
- Potential Drop-in molecular modifier without requiring expensive replacement of processing equipment

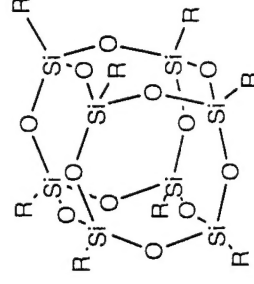
# POSS = Polyhedral Oligomeric Silsesquioxane

## General Synthesis

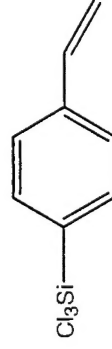
---



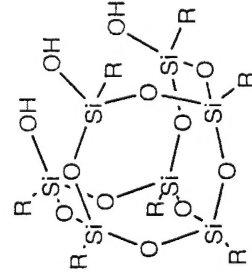
R = cyclopentyl  
vinyl



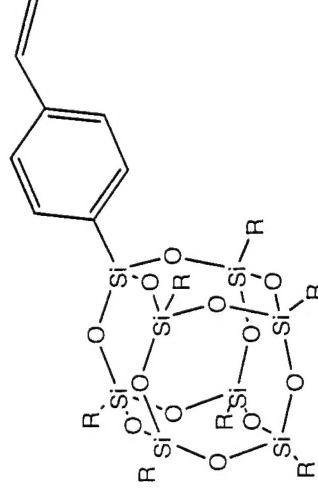
R = cyclopentyl  
vinyl



THF,  $\text{NEt}_3$  -  $\text{NEt}_3\cdot\text{HCl}$



R = cyclopentyl

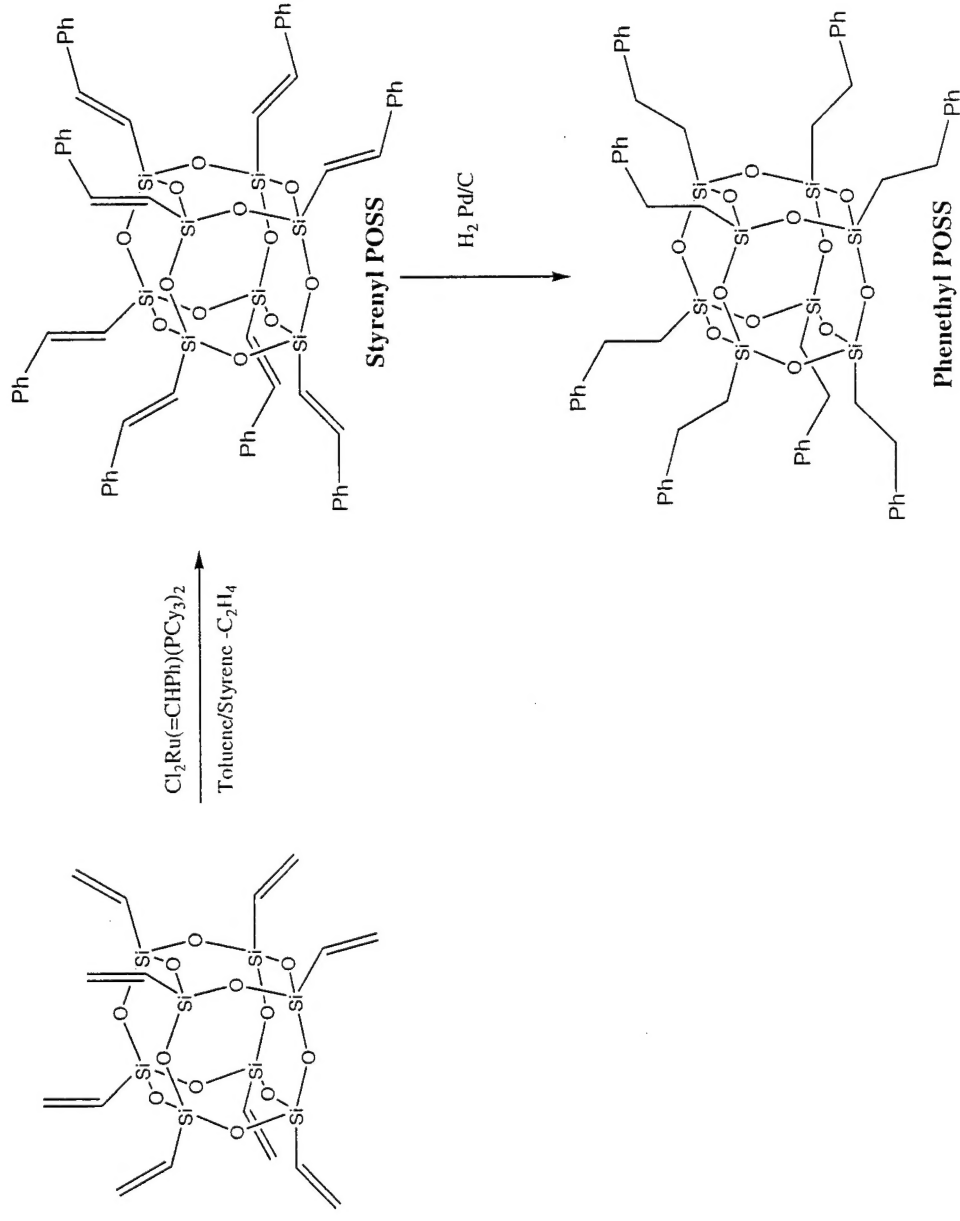


R = cyclopentyl

# POSS = Polyhedral Oligomeric Silsesquioxane

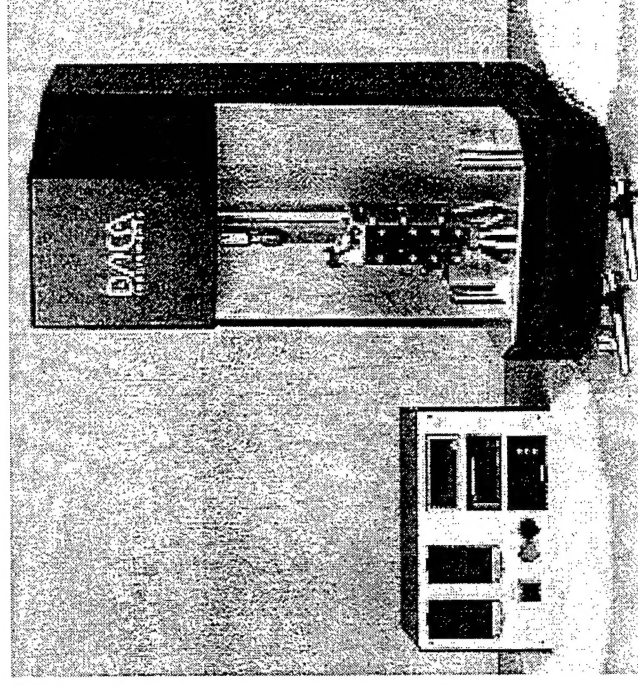
## General Synthesis

---



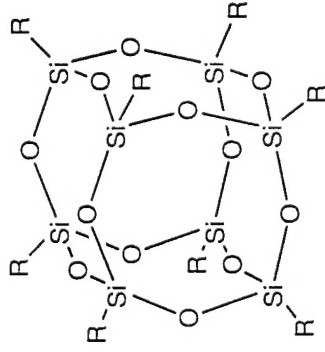
# Preparation of Styrene-POSS Blends

- TEM Method
- Dissolve the Styrene and POSS in THF
- Cast very thin film by slow solvent evaporation
- Traditional Processing
- Place Polystyrene in Extruder
- Add POSS
- Blend 2-5 Minutes



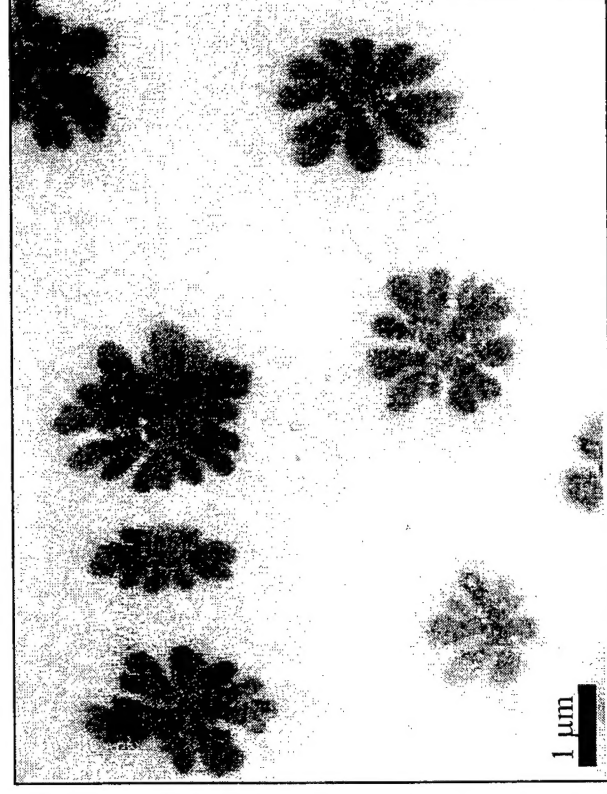
# POSS Blends - Crystal Formation

50 wt %  $\text{Cp}_8\text{T}_8$  in 2 million mol. wt. Polystyrene



R = cyclopentyl

$\text{Cp}_8\text{T}_8$

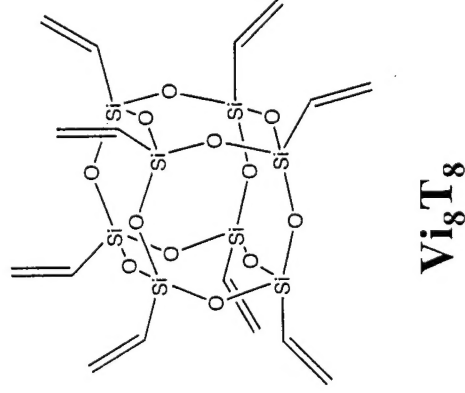


TEM image clearly shows formation of immiscible POSS crystallites (20-50k molecules)



# POSS Blends - Crystal Formation

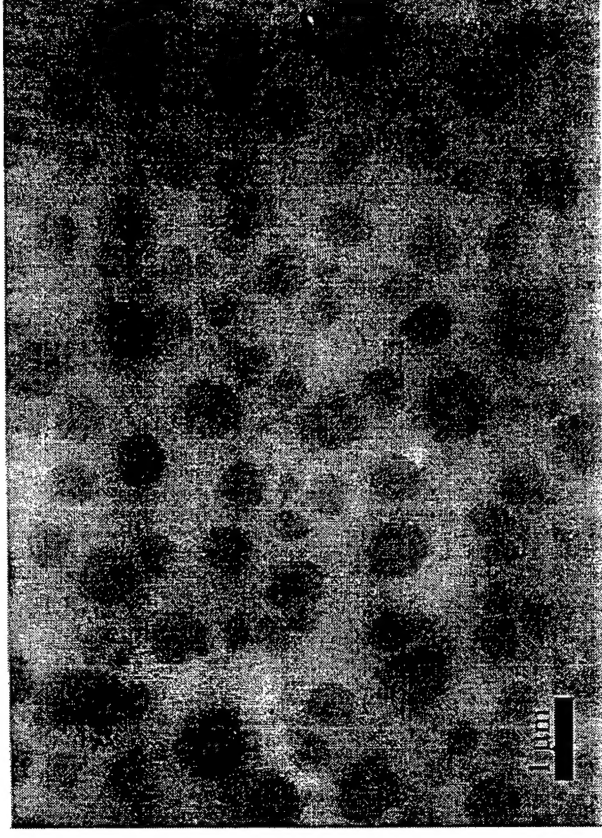
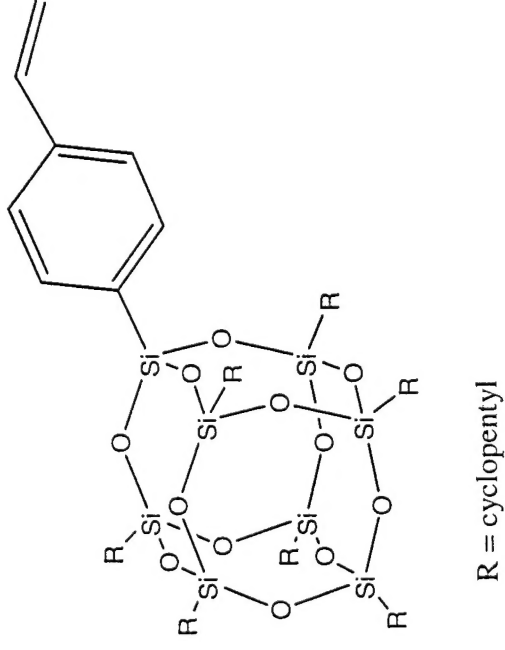
50 wt %  $\text{Vi}_8\text{T}_8$  in 2 million mol. wt. Polystyrene



TEM image clearly shows immiscibility in polymer system

# POSS Blends - Increased Solubility

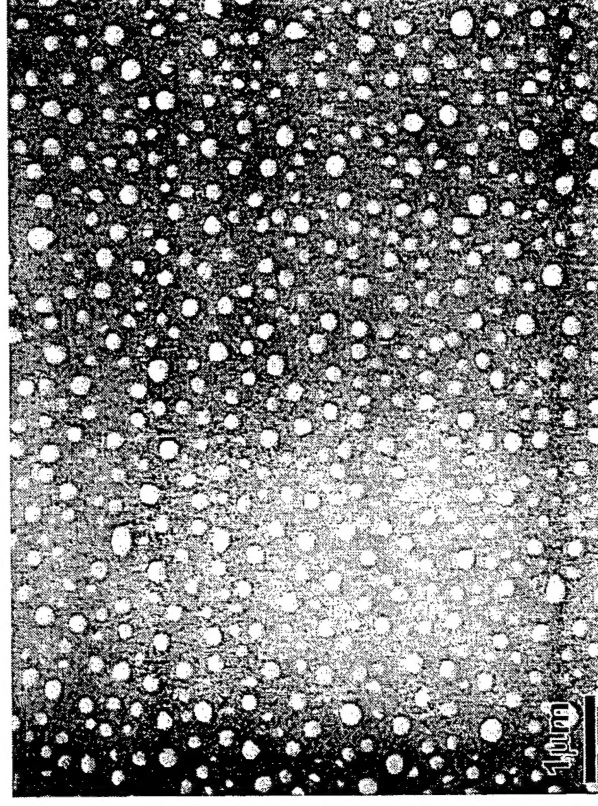
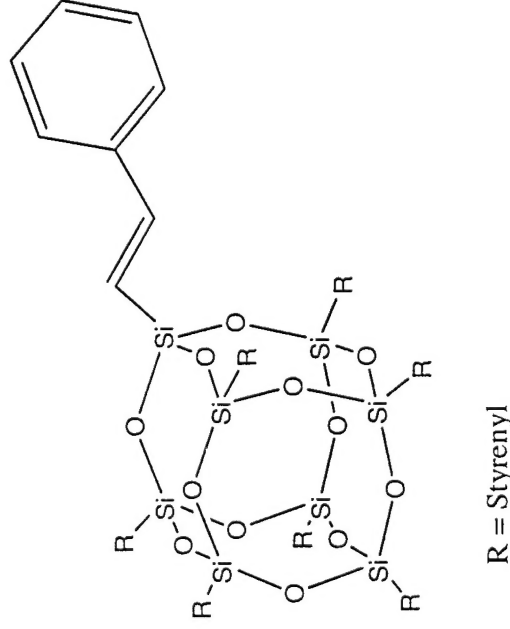
50 wt % Cp<sub>7</sub>T<sub>8</sub>Styryl in 2 million mol. wt. Polystyrene



TEM image shows significant decrease in size of crystallites

# POSS Blends - Miscibility

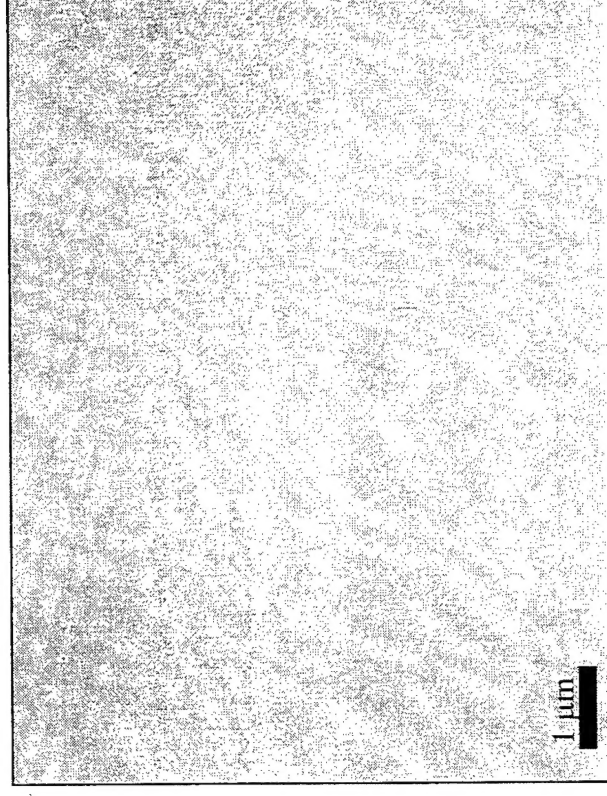
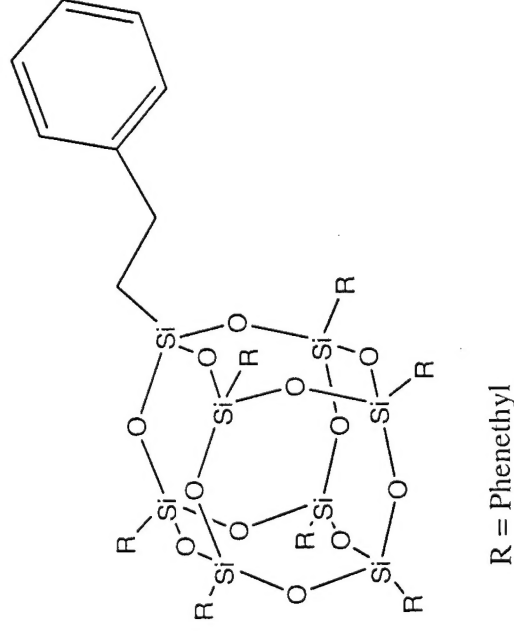
50 wt % Styrenyl<sub>8</sub>T<sub>8</sub> in 2 million mol. wt. Polystyrene



- White domains represent pure polystyrene (process issue)
- Grey domains represent miscible POSS/polystyrene
- Black dots are POSS crystallites (<100 POSS molecules)
- 30% increase in surface hardness of the material

# POSS Blends - Miscibility

50 wt % Phenethyl<sub>8</sub>T<sub>8</sub> in 2 million mol. wt. Polystyrene



- **Demonstrated Complete Miscibility!!**
- **Grey domains represent miscible POSS/polystyrene**
- **Black dots are POSS crystallites (<100 POSS molecules)**



# Conclusions

- The organic side groups on the POSS molecule are extremely important in determining the solubility of the POSS in polystyrene
- The addition of the more soluble styrenyl POSS into styrene leads to an increase in surface hardness without adversely affecting polymer properties
- POSS can be thought of as functionalized silicas with the side groups acting as solubility enhancers



# Acknowledgements

- AFRL Propulsion Directorate
- Mr. Paul Jones (Analytical)
- Dr. Charles Lee, AFOSR (Funding)